Title: P lymerized Catalyst C mp siti n

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Statement of Related Applications:

This application claims priority from USSN 60/421,282 filed October 25, 2002; USSN 60/421,163 filed October 25, 2002 and USSN 60/421,164 filed October 25, 2002. This application is related to USSN 60/434,913 filed December 20, 2003; USSN 60/435,228 filed December 20, 2003; USSN 60/435,046 filed December 20, 2003; USSN 60/433,934 filed December 17, 2003; USSN 60/434,082 filed December 17, 2003; USSN 60/446,607 filed February 11, 2003.

FIELD OF THE INVENTION

This invention relates to methods of polymerizing or oligomerizing one or more olefins using one or more activators with one or more polymerized catalyst compounds prepared by polymerizing one or more free radical polymerizable monomers (such as styrene) with one or more different olefin polymerization catalyst precursor compounds containing terminal unsaturation.

BACKGROUND

US 5,714,425 describes metallocene catalyst compositions having a polymerizable olefinic group. These metallocenes are described as being

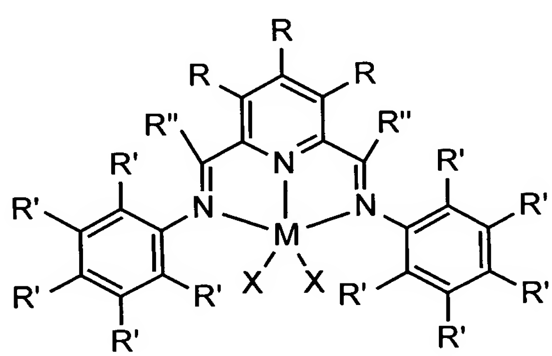
useful to prepare polyolefins. In addition, these metallocenes are described as being polymerized with one or more alpha-olefins so that the metallocene is copolymerized with the alpha-olefin. This composition is then described as useful to polymerize olefins. But US 5,714,4254 does not disclose free-radical polymerization of catalyst compositions having a polymerizable olefinic group with monomers such as styrene, isobutylene, 1,3-butadiene and the like.

US 5,679,816 discloses biscyclopentadienyl transition-metal complexes containing a conjugated diene ligand group.

US 6,150,544 and US 6,352,953 disclose bimetallic, metallacyclic catalyst compounds where one metal is a Group-4 metal and the other metal is a Group-3 metal. (Likewise, it is also known in the art to prepolymerize a heterogeneous catalyst system in the presence of at least one olefin see EPA 426,646 and US 4,871,705.)

SUMMARY

This invention relates to a composition comprising the product of combining, in the presence of a free radical initiator, one or more monomers that can be polymerized by a free radical initiator and a catalyst precursor compound represented by the formula:



wherein each X is independently a C_w hydrocarbyl group or a halogen, and M is any Group-4-11 metal, a Group-8-9 metal, or Co or Fe. R, R', and R" are independently hydrogen or C_x to C_y hydrocarbyl groups provided that at least one R' is capable of being polymerized in a polymerization process initiated by a free radical initiator.

This invention also relates to methods to polymerize olefins using the above composition.

DETAILED DESCRIPTION

Definitions

The term "hydrocarbyl radical" is sometimes used interchangeably with "hydrocarbyl" throughout this document. For purposes of this disclosure, "hydrocarbyl radical" encompasses C_1-C_{200} radicals. These radicals can be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Thus, the term "hydrocarbyl radical", in addition to unsubstituted hydrocarbyl radicals, encompasses substituted hydrocarbyl radicals, halocarbyl radicals, and substituted halocarbyl radicals, as these terms are defined below.

Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom has been replaced with a functional group such as NR''_2, OR'', PR''_2, SR'', BR''_2, SiR''_3, GeR''_3 and the like or where at least one non-hydrocarbon atom or group has been inserted within the hydrocarbyl radical, such as O, S, NR", PR", BR", SiR''_2, GeR''_2, and the like, where R" is independently a C_1-C_{30} hydrocarbyl or halocarbyl radical.

Halocarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one halogen or halogen-containing group (e.g. F, Cl, Br, I).

Substituted halocarbyl radicals are radicals in which at least one hydrocarbyl hydrogen or halogen atom has been substituted with a functional group such as NR''_2, OR'', PR''_2, SR'', BR''_2, SiR''_3, GeR''_3 and the like or where at least one non-carbon atom or group has been inserted within the halocarbyl radical such as O, S, NR", PR", BR", SiR''_2, GeR''_2, and the like where R" is independently a C_1-C_{30} hydrocarbyl or halocarbyl radical provided that at least one halogen atom remains on the original halocarbyl radical.

In some embodiments, a hydrocarbyl radical is independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl, triacontenyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, tridecynyl, tetradecynyl, pentadecynyl, hexadecynyl, heptadecynyl, octadecynyl, nonadecynyl, eicosynyl, heneicosynyl, docosynyl, tricosynyl, tetracosynyl, pentacosynyl, hexacosynyl, heptacosynyl, octacosynyl, nonacosynyl, or triacontynyl isomers. The radical may then be subjected to the types of substitutions described above.

Ancillary ligands serve to enforce the geometry around the metal center.

An "abstractable ligand" is a ligand that can be abstracted from the metal center by a cocatalyst leaving behind an activated catalyst. For

purposes of this disclosure, an "abstractable ligand" does not contain sulfur atoms; i.e. all abstractable ligands are non-sulfur-containing ligands. For purposes of this disclosure oligomers have about 2-75 mer units. In some structures throughout this specification, drawing the ligand-metal connection with an arrow, showing that the electrons for the bond originally came from the ligand, sometimes indicates coordination. At other times, drawing a solid line, showing the bond's covalent nature, indicates coordination. One of ordinary skill in the art recognizes that these depictions are interchangeable.

The term "alkyl" or "alkyl radical" refers to a branched or unbranched, saturated or unsaturated, acyclic hydrocarbyl radical. Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), vinyl, n-butyl, t-butyl, i-butyl (or 2-methylpropyl). In particular embodiments, alkyls are $C_{1\text{-}200}$ hydrocarbyls, $C_{1\text{-}50}$ hydrocarbyls, or $C_{1\text{-}20}$ hydrocarbyls.

Description

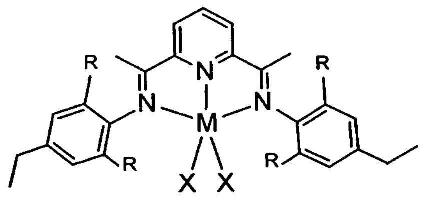
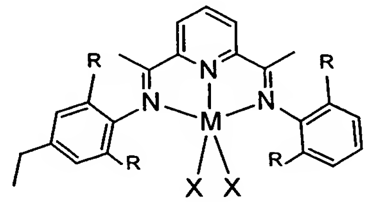
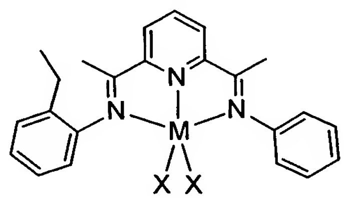
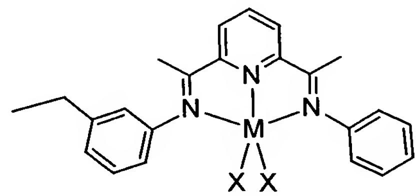
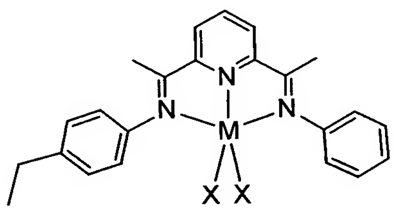
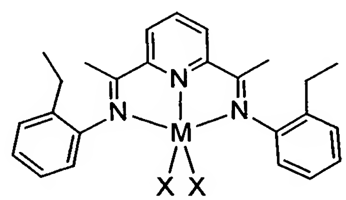
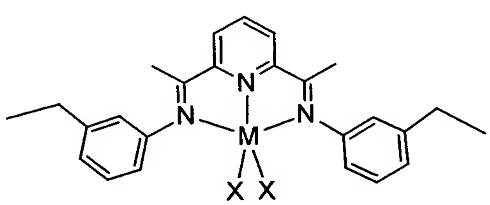
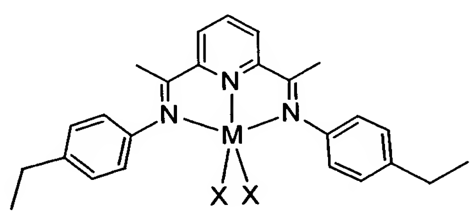
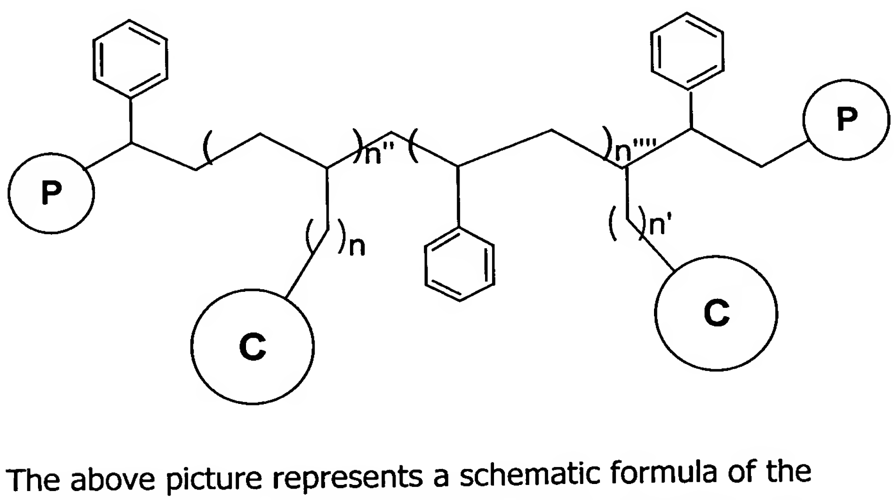
The inventive polymerized late transition metal catalyst precursors are prepared by copolymerizing Fe(II) or Co(II) pyridine diimine with an olefin such as styrene in the presence of a radical initiator (e.g., AIBN). The pyridine diimine complexes contain aryl groups that are substituted with polymerizable olefinic substituents. Divinyl benzene is optionally added to the copolymerization reaction medium to promote cross-linking.

Before polymerization into the polystyrene particle, the late transition metal catalyst precursors are sometimes simply called catalyst precursors. After polymerization, the catalyst precursors are sometimes called polymerized catalyst precursors. After activation, the polymerized catalyst precursors are sometimes called polymerized catalysts.

The inventive Fe(II) and Co(II) pyridine diimine complexes with olefinic substituents on aryl groups are synthesized. Then they are free-radical copolymerized with a simpler olefin. The resulting copolymer has units of polyolefin interspersed with enchained catalyst molecules (catalyst precursors).

In the presence of an activator, these enchained late transition metal complexes (catalyst precursors) function as ethylene polymerization or oligomerization catalysts. As shown in the Example section, aryl substituents other than the olefinic substituent sometimes affect catalyst performance.

Inventive late transition metal complexes are useful to prepare catalysts for olefin polymerization or oligomerization.

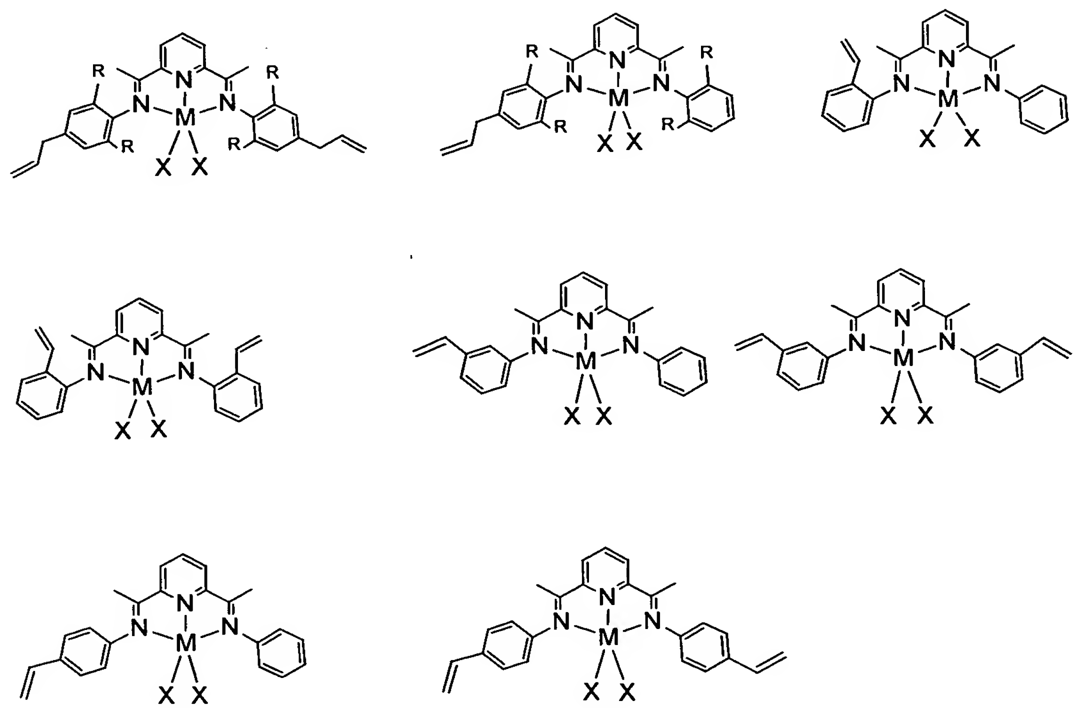
The above picture represents a schematic formula of the polymerized catalyst after polymerization. The P-labeled circles represent

the bulk polyolefin/catalyst polymer. The C-labeled circles represent the catalyst.

More than one catalyst precursor compound may be polymerized with the monomers in varying ratios.

Catalyst Compounds

Catalyst compounds useful in this invention include those represented by the formulas:



wherein each X is independently a hydrocarbyl group or a halogen, preferably a halogen, preferably chlorine; and M is any Group-4-11 metal, Group-8-9, or Co or Fe.

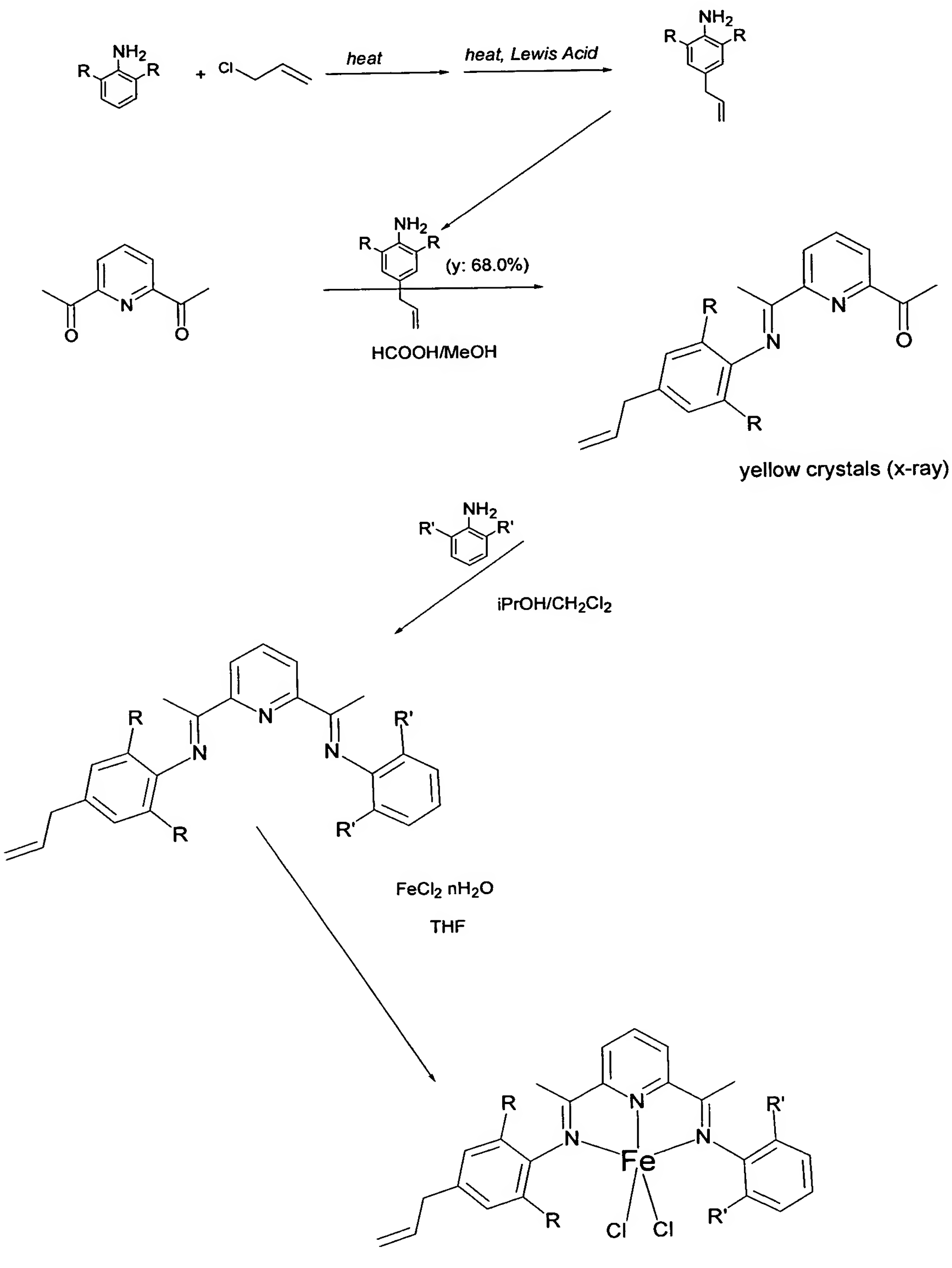
Useful catalyst c mp unds include:

2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-allylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-allylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-allylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-allylphenylimino)ethyl]pyridine cobalt dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]pyridine cobalt dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]pyridine cobalt dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinyl-2,6-

diisopropylphenylimino)ethyl]pyridine cobalt dibromide; 2-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine iron dichloride; 2-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine cobalt dichloride; 2-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine iron dibromide; 2-[1-(3-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine cobalt dibromide; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine iron dichloride; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine cobalt dichloride; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine iron dibromide; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-allylphenyliminoethyl]pyridine cobalt dibromide; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(3-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(3-vinylphenylimino)ethyl]pyridine cobalt dibromide; 2-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allylphenylimino)ethyl]pyridine cobalt dibromide; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allylphenyliminoethyl]pyridine iron dichloride; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allylphenyliminoethyl]pyridine cobalt dichloride; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allylphenyliminoethyl]pyridine iron dibromide; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-

allylphenyliminoethyl]pyridine cobalt dibromide; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(4-vinyl-2,6-diisopropylphenylimino)ethyl]-6-[1-(4-vinylphenylimino)ethyl]pyridine cobalt dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine cobalt dichloride; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dibromide; 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine cobalt dibromide

The catalyst compounds described above may be prepared according to Scheme I:



The first step in preparing invention catalysts is to prepare the ancillary ligand. The ancillary ligand can be thought of as a substituted

pyridine. In Scheme I the pyridine substituents are eth-1-yl radicals that are themselves substituted. (For purposes of this disclosure, the naming convention "eth-1-yl" means that a ethyl radical attaches to another group at the ethyl radical's 1 position; in many cases, the "-1-" portion can be omitted without loss of clarity.) The ethyl radicals substituted with an imino group; the imino group is also substituted, this time with a phenyl or substituted phenyl group. A general name for the ancillary ligand shown in Scheme I is 2-[1-(2,6-dialkylphenylimino)ethyl]-6-[1-(4-allyl-2,6-dialkyl phenylimino)ethyl]pyridine. Specifically, in Scheme I, the alkyl groups are isopropyl groups.

As the name indicates, the pyridine is substituted at its 2 and 6 positions: the square brackets set off the groups that substitute on the pyridine molecule. So, at the 2 position, pyridine is substituted with an ethyl-based radical: [1-(2,6-diisopropylphenylimino)ethyl]. Once explained, the parsing of the name leads straightforwardly to the structure. The ethyl-based radical substitutes to the pyridine through the radical's 1 position. The ethyl-based radical is a substituted ethyl radical. It is substituted at its 1 position by 2,6-diisopropylphenylimino, which is an imino radical substituted with 2,6-diisopropylphenyl.

Likewise, the substitution at the pyridine 6 position is [1-(4-allyl-2,6-diisopropyl phenylimino)ethyl]. This radical can be understood by going through the same parsing as described above. The only difference is in the phenyl group. Instead of being disubstituted, the phenyl-ring portion of the 6-position radical has an additional allyl substitutent at the phenyl ring's 4 position.

Synthesis of the ligand can occur through coupling each of the substituted phenyl ring portions to the pyridine atom in such a way that an iminoethyl connection occurs. One way of accomplishing this is shown in Scheme I. The coupling reaction is the acid-catalyzed addition of the

substituted aniline to the carbonyl groups on the pyridine (with the loss of water).

Once both substituted anilines have been added to the pyridine, synthesis of the ancillary ligand is complete. After this the ligand is simply complexed with an appropriate dicationic transition metal halide by mixing the halide and the ligand together. Specifically, in Scheme I, this metal halide is iron (II) dichloride. Thus, the overall name of the catalyst complex before it is copolymerized with an olefinic monomer is 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropyl phenylimino)ethyl]pyridine iron dichloride

Process to Prepare the Polymerized Catalyst Compounds

The catalyst precursor compound described above is then contacted with a free radical initiator and one or more monomers that can be polymerized by a free radical initiator. The catalyst compound containing the terminal unsaturation, as described above, is contacted with a free radical initiator and one or more, free-radical-polymerizable monomers.

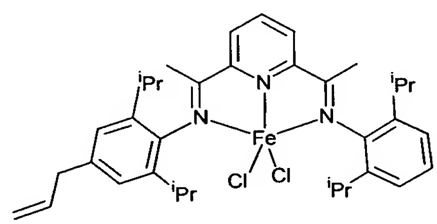
A typical late-transition metal catalyst is polymerized using the following procedure. 50 ml of a toluene solution with the terminal-unsaturation-containing catalyst, styrene, and AIBN was kept at 80 °C for 7hrs. The resulting solution was evaporated and residue was washed with dried mixture solution of hexane and toluene (2:1). The solid polymer product was collected. An analogous method was used for preparation of other polymerized catalysts

The polymerization typically takes place in solution at a temperature of 30-100 °C, 50-90°C, 70-85 °C, or 75-85 °C. Suitable solvents include toluene, benzene, xylene, and hexane. Desired solvents

are selected from those that can dissolve the terminal unsaturation-containing catalyst.

The polymerization may be performed at atmospheric, sub-atmospheric or super-atmospheric pressures.

Generally, the structure of a catalyst will look like this before copolymerization.



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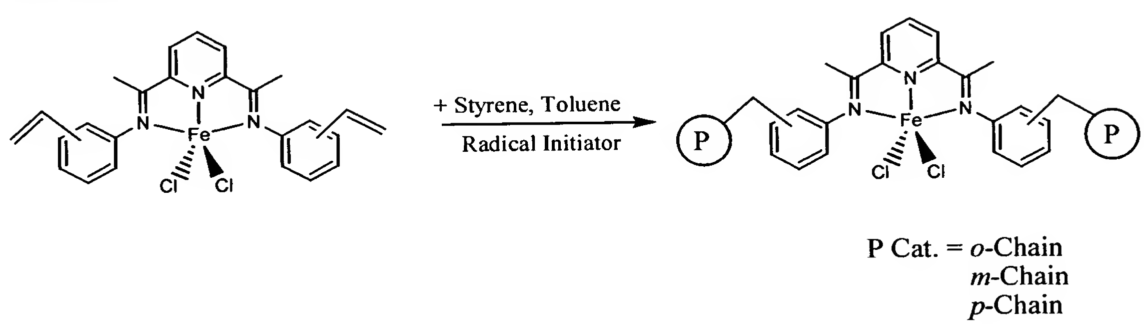
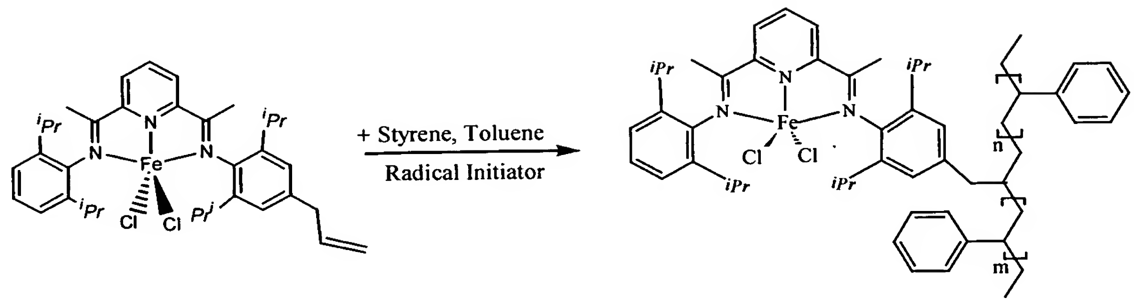
Generally, the structure of a copolymer of a catalyst and an olefin looks like this.

Scheme II



Scheme III



The polymerized catalyst compounds typically have Mw of up to 300,000; 500-150,000; 1,000-100,000; 5,000-75,000; or 10,000-50,000.

Free Radical Initiators

Free radical initiators that are useful in this invention include: (1) thermally decomposable compounds which generate radicals such as azo compounds or organic peroxides; (2) compounds which generate free radicals by non- thermal methods such as photochemical or redox processes; (3) compounds which have inherent radical character such as molecular oxygen; or (4) electromagnetic radiation such as X-rays, electron beams, visible light and ultraviolet-light. Suitable organic peroxide compounds include hydroperoxides, dialkyl peroxides, diacyl peroxides, peroxyesters, peroxydicarbonates, peroxyketals, ketone peroxides and organosulfonyl peroxides. Especially preferred peroxides are t-butyl perbenzoate, dicumyl peroxide, 2,5- dimethyl-2,5-di-tert-butylperoxy-3-hexyne (Lupersol 130), alpha,alpha.-bis(tert-butylperoxy)diisopropyl benzene (VulCup R).

Any free radical initiator or mixture having a 10-hour half-life temperature over 80° C or their mixtures may function as the initiator in invention processes to prepare supported polymerized catalyst compounds. Generally, the higher the decomposition temperature of the

peroxygen compound, the better. See pages 66-67 of Modern Plastics, November 1971 for a more complete list of such compounds.

In one embodiment, the free radical initiator is an organic peroxide compound having a half- life, at the reaction temperature, of less than one tenth of the reaction/residence time employed. The free radical initiator is used at concentrations of 1-5% weight percent based on styrene.

The following classes and examples of free-radical initiators are useful in polymerizing invention terminal-unsaturation-containing catalyst precursor compounds:

Azo initiators	Dialkyldiazenes	2,2'-azobis(2-methylpropanenitrile) (AIBN)
		1,1-azobis(1-cyclohexanenitrile)
		4,4'-azobis(4-cyanovaleric acid)
		riphenylmethylazobenzene
	Hyponitrites	di-t-butyl hyponitrite
		Dicumyl hyponitrite
Peroxides	diacyl peroxides	Dibenzoyl peroxide
		Didodecanoyl peroxide
		Diacetyl peroxide
	dialkyl peroxydicarbonates	Diisopropyl ester
		Dicyclohexyl ester
	Peresters	
	alkyl hydroperoxides	Cumyl hydroperoxide
		t-butyl hydroperoxide
	dialkyl peroxides	Dicumyl peroxide
		di-t-butyl peroxide
	inorganic peroxides	Hydrogen peroxide
		persulfate

Monomers Polymerizable by a Free Radical Initiator

Monomers that can be polymerized by a free radical process include ethylene, 1,3-butadiene, isoprene, styrene, alkyl styrene, isobutylene, vinyl chloride, vinylidene chloride, vinyl fluoride, tetrafluoroethylene, vinyl esters, acrylic esters, methacrylic esters, acrylonitrile, and propylene. Therefore, any of these can be copolymerized with the catalyst compound containing the terminal unsaturation. For example, selecting isoprene for copolymerization results in a catalyst/isoprene copolymer.

Process to Polymerize Olefins Using the Polymerized Catalyst Compound

Combining the polymerized catalyst compounds described above with one or more activators forms an olefin-polymerization catalyst system.

For purposes of this disclosure, the terms activator and cocatalyst are used interchangeably. An activator functions to remove an abstractable ligand X from the transition metal. After activation the transition metal is left with an empty coordination site at which incoming α-olefin can coordinate before it is incorporated into the oligomer or polymer. Any reagent that can so function without destroying the commercial viability of the oligomerization or polymerization process is suitable for use as an activator or cocatalyst in this invention.

Invention-suitable activators include Lewis acid, non-coordinating ionic activators or ionizing activators, or any other compound including Lewis bases, aluminum alkyls, conventional-type cocatalysts, and their combinations that can convert a catalyst compound into a catalytically active cation. This invention can use alumoxane or modified alumoxane as an activator, and can also use ionizing activators, neutral or ionic, such as tri (n-butyl) ammonium tetrakis(pentafluorophenyl) boron, a

trisperfluorophenyl boron metalloid precursor or a trisperfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), or their combinations. This invention can use these compounds as activators if they can ionize the catalyst metal compound or if the catalyst metal compound can be pre-reacted to form a compound that these activators can ionize.

One class of invention-suitable activators includes alumoxanes such as methylalumoxane, modified methylalumoxane, ethylalumoxane, etc.; aluminum alkyls such as trimethyl aluminum, triethyl aluminum, triisopropyl aluminum, etc.; alkyl aluminum halides such as diethyl aluminum chloride, etc.; and alkylaluminum alkoxides.

An alumoxane component useful as an activator is typically an oligomeric aluminum compound represented by the general formula $(R''\text{-}Al\text{-}O)_n$, which is a cyclic compound, or $R''(R''\text{-}Al\text{-}O)_nAlR''_2$, which is a linear compound. Generally, R" is independently a C_1-C_{20} alkyl radical, for example, methyl, ethyl, propyl, butyl, pentyl, isomers thereof, etc., and "n" is an integer from 1-50. Those of ordinary skill in the art recognize that alumoxanes in which R" is methyl and "n" is at least four are particularly useful: methylalumoxane and modified methylalumoxanes. For further descriptions see, EP 279586, EP 561476, WO94/10180, and US Pat. Nos. 4,665,208, 4,908,463, 4,924,018, 4,952,540, 4,968,827, 5,041,584, 5,103,031, 5,157,137, 5,235,081, 5,248,801, 5,329,032, 5,391,793, and 5,416,229.

Those of ordinary skill in the art know how to prepare alumoxanes and modified alumoxanes. See U.S. Patent No. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253, 5,731,451, 5,744,656, 5,847,177, 5,854,166, 5,856,256 and 5,939,346 and European

publications EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and EP-B1-0 586 665, and PCT publication WO 94/10180.

Another class of invention-suitable activators includes aluminum alkyl components represented by the general formula $R''AlZ_2$ where R″ is defined above for alumoxanes, and each Z is independently R″ or a different univalent anionic ligand such as halogen (Cl, Br, I), alkoxide (OR″), etc. Particularly useful aluminum alkyls include triethylaluminum, diethylaluminum chloride, triisobutylaluminum, tri-n-octylaluminum, etc.

When alumoxane or aluminum alkyl activators are used, the catalyst-precursor-to-activator molar ratio is from about 1:1000 to 10:1; alternatively, 1:500 to1:1; or 1:300 to 1:10.

Yet another class of invention-suitable activators includes discrete ionic activators. These are especially useful when both abstractable ligands are hydride or hydrocarbyl. $[Me_2PhNH][B(C_6F_5)_4]$, $[Bu_3NH][BF_4]$, $[NH_4][PF_6]$, $[NH_4][SbF_6]$, $[NH_4][AsF_6]$, $[NH_4][B(C_6H_5)_4]$ or Lewis acidic activators such as $B(C_6F_5)_3$ or $B(C_6H_5)_3$ are examples of discrete ionic activators. Discrete ionic activators provide for an activated catalyst site and a relatively non-coordinating (or weakly coordinating) anion. Activators of this type are well known, see for instance W. Beck, et al., Chem. Rev., vol. 88, p. 1405-1421 (1988); S. H. Strauss, Chem. Rev., vol. 93, p. 927-942 (1993); US Pat. Nos. 5,198,401; 5,278,119; 5,387,568; 5,763,549; 5,807,939; 6,262,202; and WO93/14132; WO99/45042; WO01/30785; and WO01/42249. These activator types also function when X is not hydrocarbyl, if they are used with a compound capable of alkylating the metal such as an alumoxane or aluminum alkyl.

When a discrete ionic activator is used, the catalyst-precursor-to-activator molar ratio is from 10:1 to 1:10; 5:1 to 1:5; 2:1 to 1:2; or 1.2:1 to 1:1.

Another class of invention-suitable activators includes those described in PCT publication WO 98/07515 such as tris(2,2',2"-nonafluorobiphenyl) fluoroaluminate. Combining activators from different classes suits this invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP-B1 0 573 120, PCT publications WO 94/07928 and WO 95/14044 and U.S. Patent Nos. 5,153,157 and 5,453,410. WO 98/09996 describes activating catalyst compounds with perchlorates, periodates, and iodates including their hydrates. WO 98/30602 and WO 98/30603 describe the use of lithium (2,2'-bisphenyl-ditrimethylsilicate)•4THF as an activator for a catalyst compound. WO 99/18135 describes the use of organo-boron-aluminum activators. EP-B1-0 781 299 describes using a silylium salt in combination with a non-coordinating compatible anion. Also, activation methods using irradiation (see EP-B1-0 615 981), electrochemical oxidation, etc., are also useful for activating catalyst precursors. Other activators or activating methods are described in, for example, U.S. Patent Nos. 5,849,852, 5,859,653 and 5,869,723 and WO 98/32775, WO 99/42467 (dioctadecylmethylammonium-bis(tris(pentafluorophenyl)borane) benzimidazolide).

Combining modified alumoxanes with invention polymerized catalyst compounds forms a catalyst system. MMAO3A (modified methyl alumoxane in heptane, commercially available from Akzo Chemicals, Inc., Holland, under the trade name Modified Methylalumoxane type 3A) is such an example. Combining the alumoxanes disclosed in U.S. Patent No. 5,041,584 with invention polymerized catalyst compounds forms a catalyst system, as well.

Polymerization Processes (TM catalyzed)

Some of the catalyst systems described above are suitable for use in solution polymerization processes, some for use in gas-phase processes, and some in slurry processes. Some of the catalyst systems above are suitable for use in combinations of those processes.

In invention polymerization or oligomerization processes using invention catalyst systems, the process temperature can be -100°C to 300°C, -20°C to 200°C, or 0°C to 150°C. Given one of these temperature ranges, the following ethylene oligomerization pressures (gauge) are useful: 0 kPa-35 MPa or 500 kPa-15 MPa.

In polymerization or oligomerization processes using invention catalyst systems and any of the process conditions described above, whether the selected process is solution, slurry, gas-phase or an amalgamation of these, the process can employ one or more, C_2-C_{30} monomers. Alternatively, C_2-C_{12} or C_2-C_8 monomers are suitable. Specific examples of invention-suitable monomers include one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, 3-methyl-pentene-1, and cyclic olefins, or their combinations. Other monomers can include vinyl monomers, diolefins such as dienes, polyenes, norbornene, norbornadiene, vinyl norbornene, ethylidene norbornene monomers. Alternatively, invention polymerization processes produce homopolymers or copolymers of ethylene or propylene.

In polymerization or oligomerization processes using invention catalyst systems and any of the process conditions described above, polymerization with ethylene and at least two different comonomers forms terpolymers. Invention comonomers comprise a combination of any of the monomers described above or of C_2-C_{30} or C_4-C_8, α-olefin monomers, optionally with at least one diene monomer. Terpolymers include

combinations such as propylene/but-1-ene/hex-1-ene, propylene/but-1-ene/ethylene, propylene/ethylene/hex-1ene, propylene/butene/norbornene, propylene/butene/decadiene, and the like. For purposes of this disclosure, nomenclature such as "but-1-ene", which indicates that the olefinic unsaturation in the butene molecule begins at the first atom in the butene carbon chain, is equivalent to "butene-1".

Invention oligomerization or polymerization processes can be run in the presence of various liquids, particularly aprotic organic liquids. In some embodiments the catalyst system is insoluble in most solvents; and thus, the polymerization will be slurry phase rather than solution phase. Liquid-suitable invention catalyst systems include alkanes, alkenes, cycloalkanes, selected halogenated hydrocarbons, aromatic hydrocarbons, and in some cases, hydrofluorocarbons. Useful solvents specifically include hexane, toluene, cyclohexane, and benzene.

Gas-phase polymerization

In polymerization or oligomerization processes using invention catalyst systems, the reactor pressure in a gas-phase process can vary from 69 kPa-3.5 MPa, alternatively from 690 kPa-3.5 MPa, from 1379 kPa-2.8 MPa, or from 1.7-2.414 MPa. Invention processes and catalyst systems can use suitable gas-phase polymerization processes; some of these processes are described below.

In gas-phase, polymerization or oligomerization processes using invention catalyst systems, given a particular reactor pressure range, the reactor temperature can vary from 30-120°C, alternatively from 60-115°C, from 70-110°C, or from 70-95°C. The reactor temperature is typically between 70-105 °C for high-density polyethylene.

In gas-phase systems, polymerization or oligomerization processes using invention catalyst systems, monomer partial pressure influences catalyst system productivity. Primary monomer concentration, such as ethylene or propylene, is from 25-90 mole percent, and its partial pressure is from 138-517kPa or 517 kPa-2.1 MPa. These conditions suit invention gas-phase, polymerization or oligomerization processes. Also, in some systems, comonomer presence yields productivity increases.

Gas-phase, polymerization or oligomerization processes using invention catalyst systems can produce 227-90,900 kg/hr of polymer, alternatively, 227-455 kg/hr, 227-4540 kg/hr, 227-11,300 kg/hr, 227-15,900 kg/hr, 227-22,700 kg/hr, and alternatively 29,000 kg/hr-45,500 kg/hr, or 45,500 kg/hr or more.

Gas-phase, polymerization or oligomerization processes using invention catalyst systems can use the processes described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200, EP-A- 0 802 202 and EP-B- 634 421.

In some gas-phase, polymerization or oligomerization processes using invention catalyst systems, the reactor receives the liquid or solution catalyst system in its liquid form at a resin-particle-lean zone. For information on how to introduce a liquid catalyst system into a fluidized bed polymerization reactor at a resin-particle-lean zone, see US 5,693,727.

Gas-phase, polymerization or oligomerization processes using invention catalyst systems can operate with scavengers. Typical scavengers include trimethyl aluminum, tri-isobutyl aluminum, an excess of alumoxane or modified alumoxane, triethylaluminum, tri-n-hexylaluminum, diethyl aluminum chloride, dibutyl zinc and the like. PCT publication WO 96/08520 and U.S. Patent No. 5,712,352 describe processes using these scavengers. Invention, gas-phase processes or

catalyst systems can use these processes. Alternatively, gas-phase, polymerization, or oligomerization processes using invention catalyst systems can operate in the absence of or essentially free of scavengers.

Slurry Polymerization

In polymerization or oligomerization processes using invention catalyst systems, slurry polymerization processes generally use pressures of 103-5068 kPa and temperatures of 0-120°C. Invention processes and catalyst systems can use suitable slurry polymerization processes; some of these processes are described below.

Typically, in a slurry polymerization, a suspension of solid, particulate polymer forms in a liquid polymerization medium to which ethylene (or α-olefinic monomer) and comonomers, along with catalyst, has been added. This suspension intermittently or continuously discharges from the reactor, after which the process separates the polymer from the volatile components and recycles them (optionally after a distillation) to the reactor. The liquid employed in the polymerization medium typically comprises a C_3-C_7 alkane, alternatively a branched alkane. The medium should be liquid and relatively inert under the polymerization conditions. For propane media, process temperatures and pressures are usually above the media's critical temperature and pressure. The processes can use hexane or isobutane media, as well.

One slurry polymerization process is a particle-form polymerization. It is a process where the temperature remains below the temperature at which the polymer appreciably dissolves in the reaction medium. Such techniques are well known in the art. U.S. Patent No. 3,248,179. Particle-form process temperatures range from 85°C-110°C. Two other slurry polymerization varieties employ a loop reactor or a plurality of stirred reactors in series, parallel, or combinations thereof. These reactors can

have cooling or not and can employ refrigerated or unrefrigerated monomer feeds. Non-limiting examples of slurry processes include continuous-loop and stirred-tank processes. Also, U.S. Patent No. 4,613,484 describes other examples of slurry processes.

Slurry processes can use a continuous-loop reactor. The process regularly injects the catalyst, as a slurry in a compatible solvent or as a dry, free-flowing powder, into the reactor loop. The loop contains a circulating slurry of growing polymer particles in a diluent of isobutane containing monomer and comonomer. If desired, this process can control molecular weight with hydrogen. The reactor is maintained at a pressure of 3.620-4.309 kPa and at a temperature of 60-104 °C depending on the desired polymer density. Reaction heat is removed from the reactor through the loop wall since much of the reactor vessel is a double-jacketed pipe. The slurry discharges from the reactor at regular intervals or continuously. It discharges into a heated, low-pressure flash vessel, rotary dryer, and nitrogen purge column, in sequence, to remove isobutane diluent and all unreacted monomer and comonomer. The resulting hydrocarbon-free powder is then compounded for use in various applications.

Polymerization or oligomerization processes using invention catalyst systems and using slurry polymerization conditions can produce 1-100,000 kg polymer/hr, 907-100,000 kg/hr, 2268-100,000 kg/hr, 4540-100,000 kg/hr, 6804-100,000 kg/hr, 11,340-100,000 kg/hr, or 45,500-100,000 kg/hr.

Polymerization or oligomerization processes using invention catalyst systems and using slurry polymerization conditions can use total reactor pressures in the range of 2758-5516 kPa, 3103-4827 kPa, 3448-4482 kPa, or 3620-4309 kPa.

Polymerization or oligomerization processes using invention catalyst systems and using slurry polymerization conditions can use concentrations of predominant monomer in the reactor liquid medium of 1-10 wt%, 2-7 wt%, 2.5-6 wt%, or 3-6 wt%.

As with gas-phase polymerization conditions, polymerization or oligomerization processes using invention catalyst systems and slurry polymerization conditions can use slurry process variants that include or exclude scavengers.

Applications of Invention Polyolefins

Invention processes prepare homo- and co-polymer polyethylene useful for formulating adhesives and other materials.

Formulations

In some embodiments, the polymer produced by this invention may be blended with one or more other polymers such as thermoplastic polymer(s) and elastomer(s).

A thermoplastic polymer is a polymer that can be melted by heating and then cooled without appreciable change in properties. Thermoplastic polymers typically include polyolefins, polyamides, polyesters, polycarbonates, polysulfones, polyacetals, polylactones, acrylonitrile-butadiene-styrene resins, polyphenylene oxide, polyphenylene sulfide, styrene-acrylonitrile resins, styrene maleic anhydride, polyimides, aromatic polyketones, or mixtures of two or more of the above. Specific polyolefins include polymers comprising one or more, linear, branched, or cyclic, C_2-C_{40} olefins, preferably polymers comprising ethylene or propylene copolymerized with one or more, C_3-C_{40} olefins, C_3-C_{20} α-olefins, or C_3-C_{10} α-olefins.

Elastomers include all natural and synthetic rubbers, including those defined in ASTM D1566. Examples of elastomers include ethylene propylene rubber, ethylene propylene diene monomer rubber, styrenic block copolymer rubbers (including SI, SIS, SB, SBS, SIBS and the like, where S=styrene, I=isobutylene, and B=butadiene), butyl rubber, halobutyl rubber, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, natural rubber, polyisoprene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, polybutadiene rubber (both cis and trans).

In another embodiment polymer produced by this invention is combined with one or more isotactic polypropylenes; highly isotactic polypropylenes; syndiotactic polypropylenes; random copolymers of propylene and ethylene or butene or hexene; polybutenes; ethylene vinyl acetate; low-density polyethylenes (density 0.915 to 0.935 g/cm^3); linear-low-density polyethylenes; ultra-low-density polyethylenes (density 0.86 to 0.90 g/cm^3); very-low-density polyethylenes (density 0.90 to 0.915 g/cm^3); medium-density polyethylenes (density 0.935 to 0.945 g/cm^3); high-density polyethylenes (density 0.945 to 0.98 g/cm^3); ethylene vinyl acetates; ethylene methyl acrylates; copolymers of acrylic acid, polymethylmethacrylate, or any other polymers polymerizable by high-pressure free radical processes; polyvinylchlorides, polybut-l-enes; isotactic polybutenes; ABS resins; ethylene-propylene rubbers (EPR); vulcanized EPRs; EPDMs; block copolymers; styrenic block copolymers; polyamides; polycarbonates; PET resins; crosslinked polyethylenes; copolymers of ethylene and vinyl alcohol (EVOH); or polymers of aromatic monomers such as polystyrene; poly-1-esters; polyacetal; polyvinylidine fluoride; polyethylene glycols; or polyisobutylenes.

In another embodiment, elastomers are blended with the polymer produced by this invention to form rubber-toughened compositions. In some embodiments, the rubber toughened composition is a two (or more) phase system where the elastomer is a discontinuous phase and the polymer produced by this invention is a continuous phase. This blend may be combined with tackifiers or other additives as is known in the art.

In another embodiment, the polymer produced by this invention may be blended to form impact copolymers. In some embodiments, the blend is a two (or more) phase system with a discontinuous phase and a continuous phase. This blend may be combined with tackifiers or other additives as is known in the art.

In some embodiments invention polymers are combined with metallocene polyethylenes (mPEs) or metallocene polypropylenes (mPPs). The mPE and mPP homopolymers or copolymers are typically produced using mono- or bis-cyclopentadienyl transition metal catalysts in combination with alumoxane or a non-coordinating anion activator in solution, slurry, high-pressure, or gas-phase conditions. The supported or unsupported catalyst and activator may have substituted or unsubstituted cyclopentadienyl rings. ExxonMobil Chemical Company (Baytown, Texas) produces several commercial products with such catalyst and activator combinations. These are commercially available under the tradenames EXCEED™, ACHIEVE™, and EXACT™. For more information on the methods and catalyst-activator pairs used to produce such homopolymers and copolymers, see WO 94/26816; WO 94/03506; EPA 277,003; EPA 277,004; U.S. Pat. No. 5,153,157; U.S. Pat. No. 5,198,401; U.S. Pat. No. 5,240,894; U.S. Pat. No. 5,017,714; CA 1,268,753; U.S. Pat. No. 5,324,800; EPA 129,368; U.S. Pat. No. 5,264,405; EPA 520,732; WO 92 00333; U.S. Pat. No. 5,096,867; U.S. Pat. No. 5,507,475; EPA 426 637;

EPA 573 403; EPA 520 732; EPA 495 375; EPA 500 944; EPA 570 982; WO91/09882; WO94/03506 and U.S. Pat. No. 5,055,438.

In some embodiments invention polymers are present in the above blends, at from 10-99 wt%, 20-95 wt%, 30-90 wt%, 40-90 wt%, 50-90 wt%, 60-90 wt%, 70-90 wt%. (Based upon the weight of the polymers in the blend.)

The blends described above may be produced by mixing the invention polymers with one or more polymers (as described above), by connecting reactors together in series to make reactor blends, or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together before being put into the extruder or may be mixed in the extruder.

Any of the above polymers may be functionalized, which means that the polymer has been reacted with an unsaturated acid or anhydride. Unsaturated acids and anhydrides include any unsaturated organic compound containing at least one double bond and at least one carbonyl group. Representative acids include carboxylic acids, anhydrides, esters and their metallic and non-metallic salts. In some embodiments the organic compound contains an ethylenic unsaturation conjugated with a carbonyl group (-C=O). Examples include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, alpha.methyl crotonic, and cinematic acids as well as their anhydrides, esters and salt derivatives. The unsaturated acid or anhydride is present at 0.1-10 wt%, 0.5-7 wt% or 1-4 wt%, based upon the weight of the hydrocarbon resin and the unsaturated acid or anhydride.

Tackifiers may be blended with invention polymers or with blends of invention polymers (as described above). Examples of useful tackifiers include aliphatic hydrocarbon resins, aromatic modified aliphatic

hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, hydrogenated terpenes and modified terpenes, and hydrogenated rosin esters. In some embodiments, the tackifier is hydrogenated. In other embodiments, the tackifier is non-polar. (Non-polar means that the tackifier is substantially free of monomers having polar groups. Some tackifier compositions limit the polar-group content to 5 wt% or less, alternatively, 2 or 0.5 wt% or less.) In some embodiments the tackifier has a softening point (Ring and Ball, as measured by ASTM E-28) of 80-40 or 100-30 °C. In some embodiments, the tackifier is functionalized, which means that the hydrocarbon resin has been contacted with an unsaturated acid or anhydride. Some embodiments select unsaturated acids or anhydrides from any unsaturated organic compound containing at least one double bond and at least one carbonyl group. Representative acids include carboxylic acids, anhydrides, esters and their salts, both metallic and non-metallic. In some embodiments the organic compound contains an ethylenic unsaturation conjugated with a carbonyl group (-C=O). Examples include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, alpha.methyl crotonic, and cinnamic acids as well as their anhydrides, esters and salt derivatives. The unsaturated acid or anhydride is present at 0.1 wt%, alternatively 0.5 wt% or 1 wt%, based upon the weight of the hydrocarbon resin and the unsaturated acid or anhydride.

Invention polymers, or their blends, may further comprise a crosslinking agent. Particularly suitable crosslinking agents include those having functional groups that can react with the acid or anhydride group. Alcohols, multiols, amines, diamines, and triamines belong to a

nonexclusive list of crosslinking agents. Examples of useful crosslinking agents include polyamines such as ethylenediamine, diethylenetriamine, hexamethylenediamine, diethylaminopropylamine, and menthanediamine.

Invention polymers, or their blends, may further comprise typical additives known in the art such as fillers, cavitating agents, antioxidants, surfactants, adjuvants, plasticizers, antiblock additives, color masterbatches, pigments, dyes, processing aids, UV stabilizers, neutralizers, lubricants, waxes, or nucleating agents. Typically, these additives are present in amounts well known to be effective in the art: such as 0.001-10 wt%.

Specific fillers, cavitating agents, or nucleating agents include titanium dioxide, calcium carbonate, barium sulfate, silica, silicon dioxide, carbon black, sand, glass beads, mineral aggregates, talc, clay, etc.

Effective antioxidants include phenolic antioxidants, such as Irganox 1010, Irganox, 1076 both available from Ciba-Geigy. Effective oils include paraffinic or naphthenic oils, such as Primol 352 or Primol 876 available from ExxonMobil Chemical France, S.A. (Paris, France) and aliphatic naphthenic oils, white oils, etc.

Effective plasticizers and adjuvants include mineral oils, polybutenes, phthalates, etc. Plasticizers include phthalates such as diisoundecyl phthalate (DIUP), diisononylphthalate (DINP), dioctylphthalates (DOP), and polybutenes.

Effective processing aids, lubricants, waxes, and oils include low molecular weight products such as wax, oil or low Mn polymer, (low meaning Mn below 5000, below 4000, below 3000, or below 2500). Effective waxes include polar or non-polar waxes, functionalized waxes, polypropylene waxes, polyethylene waxes, and wax modifiers. Effective

functionalized waxes include those modified with an alcohol, an acid, or a ketone.

Some invention polymers are functionalized after polymerization. Functionalized means that the polymer has been contacted with an unsaturated acid or anhydride. Suitable unsaturated acids or anhydrides include any unsaturated organic compound comprising one double bond and one carbonyl group. Representative acids include carboxylic acids, anhydrides, esters and their salts, both metallic and non-metallic. Some useful organic compound contains an ethylenic unsaturation conjugated with a carbonyl group (-C=O). Examples include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, alpha.methyl crotonic, and cinnamic acids as well as their anhydrides, esters and salt derivatives. The unsaturated acid or anhydride is present at 0.1-10 wt%, alternatively 0.5-7 wt% or 1-4 wt% based upon the weight of the hydrocarbon resin and the unsaturated acid or anhydride. Specific examples include waxes modified by methyl ketone, maleic anhydride, or maleic acid. Suitable low Mn polymers include lower α-olefins polymers such as propylene, butene, pentene, hexene, etc. Some embodiments select the polymer such that it includes polybutene having an Mn of less than 1000.

APPLICATIONS

Invention polymers (and their blends as described above) whether formed in situ or by physical blending are used in any known thermoplastic or elastomer application. Examples include uses in molded parts, films, tapes, sheets, tubing, hose, sheeting, wire and cable coating, adhesives, shoe soles, bumpers, gaskets, bellows, films, fibers, elastic fibers, nonwoven materials, spunbond materials, sealants, surgical gowns, and medical devices.

Adhesives

Invention polymers or their blends can be used as adhesives, either alone or combined with tackifiers. Preferred tackifiers are described above. The tackifier is typically present at about 1 wt% to about 50 wt%, based upon the weight of the blend, more preferably 10 wt% to 40 wt%, even more preferably 20 wt% to 40 wt%. Other additives, as described above, may be added also.

Invention-polymer-based adhesives can be used in any adhesive application, such as disposable items, packaging, laminates, pressure-sensitive adhesives, tapes labels, wood binding, paper binding, non-woven materials, road marking materials, reflective coatings, etc. In some embodiments Invention-polymer-based adhesives can be used for chassis construction in disposable diapers and napkins, elastic attachment in disposable-goods, and converting, packaging, labeling, bookbinding, woodworking, and other assembly applications. Specific articles include diaper liquid-transfer layers, diaper leg elastics, diaper frontal tapes, diaper standing-leg cuffs, feminine-napkin adhesive strips and perishable product packaging. Specific applications include laminations for diaper outer covers, diaper elastic cuffs, filter materials, filter masks, surgical gowns, and surgical drapes; core stabilization for diapers and feminine-napkins; diaper chassis construction; and filtration system bonding.

The invention-polymer-based adhesives described above may be applied to any substrate. Useful substrates include wood, paper, cardboard, plastic, thermoplastic, rubber, metal, metal foil (such as aluminum foil and tin foil), metallized surfaces, cloth, non-woven cloth (particularly polypropylene cloths), spunbonded fiber, cardboard, stone, plaster, glass (including silicon oxide (SiO_x) coatings applied by evaporating silicon oxide onto a film surface), foam, rock, ceramic, film, polymer foam (such as polyurethane foam), coated substrate (such as

those coated with inks, dyes, pigments), polyvinylidene chloride, etc. or their combinations. Additional useful substrates include polyethylene, polypropylene, polyacrylates, acrylics, polyethylene terephthalate, or any of the polymers listed above as suitable for blends. Any of the above substrates may be modified by corona treatment, electron beam irradiation, gamma irradiation, microwave, or silanization.

Films

Invention polymers and their blends can form mono- or multi-layer films. These films may be formed by any of the conventional techniques known in the art including extrusion, co-extrusion, extrusion coating, and lamination, blowing and casting. These films may be formed by the flat film or tubular process; afterwards they may be oriented in a uniaxial or in two mutually perpendicular directions in the film's plane. One or more of the layers of the film may be oriented in the transverse or longitudinal directions to the same or different extents. This orientation may occur before or after bringing the individual layers together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer, or the polyethylene and polypropylene can be coextruded into a film, then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene. Further orientation could follow, if desired. Film orientation in the machine direction (MD) is typically at a ratio of 1-15 or 5-7, while orientation in the transverse direction (TD) is typically at a ratio of 1-15 or 7-9. But in some embodiments, MD and TD orientation ratios are the same.

In another embodiment, the layer comprising the invention polymer compositions (or their blends) may be combined with one or more other layers. The other layer(s) may be any of those layers typically included in

multilayer films. For example, the other layer or layers may be polyolefins (such as homopolymers or copolymers of C_2-C_{40} olefins or C_2-C_{20} olefins) or copolymers of α-olefins and other olefins (including α-olefins and ethylene). Specific polyolefins for use as other layers include homopolyethylene; homopolypropylene; propylene copolymerized with ethylene or butene; and ethylene copolymerized with one or more of propylene, butene or hexene, and optional dienes. Specific examples include thermoplastic polymers such as ultra-low-density polyethylene, very-low-density polyethylene, linear-low-density polyethylene, low-density polyethylene, medium-density polyethylene, high-density polyethylene, polypropylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, butene, hexene, elastomers such as ethylene propylene rubber, ethylene propylene diene monomer rubber, neoprene, and blends of thermoplastic polymers and elastomers, such as for example, thermoplastic elastomers and rubber toughened plastics.

Likewise, the other layer or layers may be polar polymers. Specific polar polymers include homopolymers and copolymers of esters, amides, acetates, anhydrides, copolymers of C_2-C_{20} olefins (such as ethylene and/or propylene and/or butene with one or more polar monomers such as acetates, anhydrides, esters, alcohol, or acrylics). Specific examples include polyesters, polyamides, ethylene-vinyl-acetate copolymers, and polyvinyl chloride.

Likewise, the other layer or layers may be cationic polymers. Specific cationic polymers include polymers or copolymers of geminally disubstituted olefins, α-heteroatom-olefins, or styrenic monomers. Specific geminally disubstituted olefins include isobutylene, isopentene, isoheptene, isohexane, isooctene, isodecene, and isododecene. Specific α-heteroatom-olefins include vinyl ether and vinyl carbazole. Specific

styrenic monomers include styrene, alkyl styrene, para-alkyl styrene, α-methyl styrene, chloro-styrene, and bromo-para-methyl styrene. Specific examples of cationic polymers include butyl rubber, isobutylene copolymerized with para methyl styrene, polystyrene, and poly-α-methyl styrene.

Finally, other specific layers can be paper, wood, cardboard, metal, metal foils (such as aluminum foil and tin foil), metallized surfaces, glass (including silicon oxide (SiO_x) coatings applied by evaporating silicon oxide onto a film surface), fabric, spunbonded fibers, and non-wovens (particularly polypropylene spun bonded fibers or non-wovens), and substrates coated with inks, dyes, pigments, polyvinylidene chloride and the like.

The films may vary in thickness depending on the intended application; films from 1-250 μm thick are usually suitable. Packaging films are usually from 10-60 μm thick. Sealing layers are typically 0.2-50 μm. There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface. Additives such as antiblock additives, antioxidants, pigments, fillers, processing aids, UV stabilizers, neutralizers, lubricants, surfactants and/or nucleating agents may also be present in one or more layers in the films. Specific additives include silicon dioxide, titanium dioxide, polydimethylsiloxane, talc, dyes, wax, calcium stearate, carbon black, low-molecular-weight resins, and glass beads. In some embodiments one or more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, or microwave. In some embodiments one or both of the surface layers is modified by corona treatment.

The films described herein may also comprise from 5-60 wt% of a hydrocarbon resin, based upon the weight of the polymer and the resin. The resin may be combined with the polymer of the seal layer(s) or may

be combined with the polymer in the core layer(s). The resin softening point is 100-200 °C or 130-180°C. Preferred hydrocarbon resins include those described above. The films comprising a hydrocarbon resin may be oriented in uniaxial or biaxial directions to the same or different degrees.

The films described above may be used as stretch or cling films. Stretch-cling films are used in various bundling, packaging and palletizing operations. A number of well-known tackifying additives impart cling properties to or improve the cling properties of a particular film. Common tackifying additives include polybutenes, terpene resins, alkali metal stearates, and hydrogenated rosins and rosin esters. Corona discharge can also modify film properties. Some polymers (such as ethylene-methylacrylate copolymers) do not need cling additives and can be used as cling layers without tackifiers. Stretch-clings films may comprise a slip layer comprising any suitable polyolefin or combination of polyolefins such as polyethylene, polypropylene, copolymers of ethylene and propylene, and polymers obtained from ethylene or propylene copolymerized with minor amounts of other olefins, particularly C_4-C_{12} olefins. Polypropylene and linear low density polyethylene (LLDPE) work well. Suitable polypropylene is normally solid and isotactic (greater than 90% hot heptane insolubles) and has wide ranging melt flow rates (0.1-300 g/10 min). Additionally, the slip layer may include one or more, anti-cling (slip or antiblock) additives that may be added during polyolefin production blended in afterwards to improve the layer's slip properties. Such additives are well-known in the art and include, for example, silicas, silicates, diatomaceous earths, talcs, and various lubricants. These additives are typically used in amounts ranging from 100-20,000 ppm or 500-10,000 ppm by weight based upon the weight of the slip layer. The slip layer may, if desired, also include one or more other additives as described above.

Polymer products can be used for nonwovens, sealing layers, oriented polypropylene, and high-clarity thermoforming materials.

Low molecular weight varieties of high-pressure propylene homo- and co-polymers can be used for hot melt and pressure sensitive adhesives.

Invention processes can use finely divided, supported catalysts to prepare propylene/1-hexene copolymers with greater than 1.0 mole% hex-1-ene. In addition to finely divided supports, invention processes can use fumed silica supports in which the support particle size is small enough to form a colloid in the reaction media.

<u>End Use Articles</u>

Laminates comprising invention polymers can be used as a thermoformable sheet where the substrate is either sprayed or injection molded to couple it with the ionomer/tie-layer laminate sheet. The composite if formed into the desired shape to form the article, or composite article. Various types of substrate materials to form highly desirable articles. The laminate can be used with plastic substrates such as homopolymers, copolymers, foams, impact copolymers, random copolymers, and other applications. Specifically, some articles in which the present invention can be incorporated are the following: vehicle parts, especially exterior parts such as bumpers and grills, rocker panels, fenders, doors, hoods, trim, and other parts can be made from the laminates, composites and methods of the invention.

Other articles can also be made, for example, counter tops, laminated surface counter tops, pool liners, pool covers, boat covers, boat sails, cable jacketing, motorcycles, snowmobiles, outdoor vehicles, marine boat hulls, canoe interiors and exteriors, luggage, clothing, fabric

(combined with non-wovens), tent materials, GORETEX, Gamma-radiation resistant applications, electronic housings (TV's, VCR's and computers), wood replacement for decks and other outdoor building materials, prefab buildings, synthetic marble panels for construction, wall coverings, hopper cars, floor coating, polymer-wood composites, vinyl tiles, bath, shower, toilet applications and translucent glass replacement, sidings, lawn and outdoor furniture, appliances such as refrigerators, washing machines, etc., child toys, reflective signage and other reflective articles on roads and clothing, sporting equipment such as snowboards, surfboards, skis, scooters, in-line skate wheels, scratch resistant CD's, stadium seats, aerospace reentry shields, plastic paper goods, sports helmets, plastic microwaveable cookware, and other applications for coating plastics and metal where a highly glossy and scratch resistant surface is desirable, while not being subject to algae or discoloration.

Invention copolymers are suitable for applications such as molded articles, including injection and blow molded bottles and molded items used in automotive articles, such as automotive interior and exterior trims. Examples of other methods and applications for making these polymers and for which these polymers may be useful are described in the Encyclopedia of Chemical Technology, by Kirk-Othmer, Fourth Edition, vol. 17, at pages 748-819. When the application is for molded articles, the molded articles may include a variety of molded parts, particularly molded parts related to and used in the automotive industry, such as for example bumpers, side panels, floor mats, dashboards and instrument panels. Foamed articles are another application and examples where foamed plastics, such as foamed polypropylene, are useful may be found in Encyclopedia of Chemical Technology, by Kirk-Othmer, Fourth Edition, vol. 11, at pages 730-783. Foamed articles are particularly useful for construction and automotive applications. Examples of construction applications include heat and sound insulation, industrial, and home

appliances, and packaging. Examples of automotive applications include interior and exterior automotive parts, such as bumper guards, dashboards, and interior liners.

Invention polyolefin compositions are suitable for such articles as automotive components, wire and cable jacketing, pipes, agricultural films, geomembranes, toys, sporting equipment, medical devices, casting and blowing of packaging films, extrusion of tubing, pipes and profiles, sporting equipment, outdoor furniture (*e.g.*, garden furniture) and playground equipment, boat and water craft components, and other such articles. In particular, the compositions are suitable for automotive components such as bumpers, grills, trim parts, dashboards and instrument panels, exterior door and hood components, spoiler, wind screen, hub caps, mirror housing, body panel, protective side molding, and other interior and external components associated with automobiles, trucks, boats, and other vehicles.

Other useful articles and goods may be formed economically by the practice of this invention include crates, containers, packaging, labware, such as roller bottles for culture growth and media bottles, office floor mats, instrumentation sample holders and sample windows; liquid storage containers such as bags, pouches, and bottles for storage and IV infusion of blood or solutions; packaging material including those for any medical device or drugs including unit-dose or other blister or bubble pack as well as for wrapping or containing food preserved by irradiation. Other useful items include medical tubing and valves for any medical device including infusion kits, catheters, and respiratory therapy, as well as packaging materials for medical devices or food which is irradiated including trays, as well as stored liquid, particularly water, milk, or juice, containers including unit servings and bulk storage containers as well as transfer means such as tubing, pipes, and such.

EXAMPLES

Catalyst production

Synthesis of 4-allyl-2,6-diisopropyl aniline

A solution containing 2,6-diisopropyl aniline (35.4 g, 0.2 mol) and allyl chloride (7.6 g, 0.10 mol) was refluxed for 12 hr and then poured into water (400 ml). Adding an aqueous NaOH solution to the reaction mixture made the mixture basic. After extraction with diethyl ether (3×50 ml) and distillation (73.25 Pa, 92°C), 18.33g (84.3%) of N-allyl-2,6-diisopropyl aniline was isolated. N_d^{30}=1.5205. ^{1}H-NMR (ppm,$CDCl_3$): δ = 7.10(d, 2H, Ph-Hm), 6.81(t, 1H ,Ph-Hp), 6.05(m, 1H, CH=C), 5.34(d, 1H, C=C-H_{trans}), 5.16(d, 1H ,C=C-H_{cis}), 3.71(broad, 1H ,NH), 3.50(d, 2H ,CH_2-C=C), 3.26(m, 2H ,$CH(Me)_2$), 1.28(d, 12H ,$C=C(CH_3)_2$).

N-allyl-2,6-diisopropyl aniline (18.33 g, 0.084 mol) and $ZnCl_2$ (13.6 g, 0.1 mol) were added to a 100 ml toluene solution. This solution was refluxed for 5 hr and then poured into a NaOH aqueous solution. Extraction with Et_2O (3×50 ml) and distillation (79.93 Pa, 98°C) yielded 13.0 g (70.9%) of 4-allyl-2,6-diisopropyl aniline. N_d^{30}=1.5340, ^{1}H-NMR (ppm,$CDCl_3$): δ = 6.85(s, 2H, Ph-Hm),5.98(m, 1H, CH=C),5.09(d, 1H, C=C-H_{trans}),5.03(d, 1H, C=C-H_{cis}),3.6(br, 2H, NH_2), 3.30(d, 2H, CH_2-C=C), 2.92(m, 2H, $CH(Me)_2$), 1.26(d, 12H, $C(CH_3)_2$)

Synthesis of 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine: Ligand I

2,6-diacetylpyridine (0.3 g, 1.84 mmol) and 2,6-diisopropylaniline (0.326, 1.84 mmol) were dissolved in 50 ml dry methanol. 2ml formic acid was added as a catalyst, and the solution was stirred at room temperature for two days. The yellow solid (0.516 g, 87.1%) was collected by

filtration, washed with cold methanol, and identified as the desired monoimine by ^{1}H-NMR. This monoimine (0.5 g, 1.55 mmol) was dissolved in 25 ml hot methanol were added. 5 ml CH_2Cl_2, 2 ml formic acid, and excess 4-allyl-2,6-diisopropylaniline were then added to the monoimine. The solution was stirred in a sealed flask at 50 °C for 2 days, and yielded 0.649 g (80.4%) yellow solid. ^{1}H-NMR (ppm, $CDCl_3$): 8.46-8.50(br, 2H), 7.90-7.96(br, 1H), 7.17(d, 2H), 7.11(t, 1H), 6.98(s, 2H), 6.05(br, 1H), 5.10(t, 2H), 3.41(d, 2H), 2.77(br, 4H), 2.27(s, 6H), 1.14-1.17(br, 24H). IR(KBr cm^{-1}): 3078w, 2962s, 2926w, 2867w, 1639s, 1567m, 1460s, 1365s, 1248m, 1209m, 1120s, 995w, 834m, 802w, 794w, 774w, 737w.

Synthesis of 2,6-bis[1-(4-allyl-2,6-diisopropylphenylimino)ethyl] pyridine

A solution containing 2,6-diacetylpyridine (0.30 g, 1.84 mmol), 4-allyl-2,6-diisopropylaniline (0.80 g, 3.68 mmol), and formic acid (2 ml) in 30 ml dry methanol was refluxed under argon for 14 hours. Yellow solid was collected by filtration and washed with cold methanol (3×5 ml). Recrystallization from CH_2Cl_2:hexane (1:4) yielded 0.70 g (68%) of yellow, 2,6-bis[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine crystals. IR (KBr): ν(C=N) 1639 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 8.47(d, 2H, Py-Hm), 7.92(t, 1H, Py-Hp), 6.98(s, 4H, Ph-Hm), 6.04(m, 2H, CH=C), 5.12(m, 4H, $C=CH_2$), 3.40(d, 4H, CH_2-C=C), 2.75(m, 4H, $CH(Me)_2$), 2.27(s, 6H, CH_3), 1.15(d, 24H, $C(CH_3)_2$); ^{13}C-NMR($CDCl_3$): 167.04(C=N), 155.15(Py-C), 144.57(Ph-C), 138.12(Ph-C), 136.79(Py-C), 135.69(Ph-C), 134.75(-CH=), 123.16(Py-C), 122.12(Ph-C), 115.34(=CH_2), 40.25(-CH_2-), 28.31($C(Me)_2$), 23.24(CH_3), 22.92(CH_3), 17.14(CH_3). $C_{39}H_{51}N_3$ (561.86 g·mol-1): Anal. Calcd: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.03; H, 9.13; N, 7.55.

Synthesis f 2-[1-(2,6-diis pr pylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopr pylphenylimin)ethyl]pyridine Ir n Dichl ride: Catalyst I

2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dichloride was synthesized by adding $FeCl_2 \cdot 4H_2O$ to a THF solution of Ligand I: 2-[1-(2,6-diisopropyl phenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine. The complexing reaction proceeded with good yield. IR(KBr pellet): 3074w, 2962s, 2926w, 2868w, 1637w, 1619w, 1584m, 1465s, 1370s, 1268m, 1213m, 914m, 834w, 802w, 774m, 737w, 719w. EI-MS (70 eV): m/e = 522(M+ -FeCl2, 100%), 576(M+ -2Cl, 20%).

Synthesis of 2-[1-(phenylimino)ethyl]-6-[1-(4-allylphenylimino)ethyl]pyridine Iron Dichloride: Catalyst IA

This complex was prepared similarly to that of the diisopropyl analog (Catalyst I) except that unsubstituted aniline was used instead of 2,6-diisopropyl aniline. This replacement occurs in the synthesis of the 4-allyl- aniline and in the synthesis of the Ligand-I-type iminoethyl-4-allyl-iminoethyl-pyridines, both of which are precursors to this catalyst.

Synthesis of 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(4-allyl-2,6-dimethylphenylimino)ethyl]pyridine Iron Dichloride: Catalyst IB

This complex was prepared similarly to that of the diisopropyl analog except that 2,6-dimethyl aniline was used instead of 2,6-diisopropyl aniline, as above. This replacement occurs in the synthesis of the 4-allyl-aniline and in the synthesis of the Ligand-I-type ligand dialkyliminoethyl-4-

allyl-dialkyliminoethyl-pyridines, both of which are precursors to this catalyst.

See Table 3 for an illustration of the behavior of Catalysts I-IB under polymerization conditions.

Synthesis of 2,6-bis[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dichloride: Catalyst II

A solution containing $FeCl_2 \cdot 4H_2O$ (0.20 g, 1.00 mmol) and 2,6-bis[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine (0.60 g, 1.07 mmol) in 40 ml THF was stirred for 5 hr and then evaporated in a vacuum. The residue was washed with ether (3×10 ml), and recrystallized from CH_2Cl_2:hexane (3:1) at -20 °C to afford blue crystals of 2,6-bis[1-(4-allyl-2,6-diisopropylphenylimino)ethyl]pyridine iron dichloride (0.66g, 95.9%). IR(KBr): v(C=N) 1621 cm^{-1}. EI-MS (70 eV): m/e 653(M+ -Cl, 10), 562(M+ -$FeCl_2$ 100), 520(M+ -$FeCl_2$-C_3H_6, 5). $C_{39}H_{51}N_3FeCl_2$ (688.61 $g \cdot mol^{-1}$): Anal. Calcd: C, 68.03; H, 7.47; N, 6.10. Found: C, 67.70; H, 7.39; N, 6.13.

Catalyst Polymerization

Preparation of Polymerized Late-transition metal (Fe): Catalyst III

A solution containing 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(4-allyl-2,6-diisopropyl phenylimino)ethyl]pyridine iron dichloride (Catalyst I) (0.50g, 0.77 mmol), styrene (4ml) and AIBN (0.06g) in 50 ml toluene was maintained at 80° for 7 hrs. The resulting solution was evaporated, and the resulting residue was washed with a dried mixture of hexane and toluene (2:1). The solid polymer product was collected.

Preparati n f P lymerized Late-transiti n metal (Fe) catalyst: Catalyst IV

A solution containing 2,6-bis[(4-allyl-2,6-diisopropylphenylamino)ethyl]pyridine iron dichloride (Catalyst II) (0.34 g, 0.49 mmol), styrene (5 ml) and AIBN (0.20 g, 1.22 mmol) in 30 ml toluene was stirred, under argon, at 79-80 °C for 8 hr. The solution was evaporated under reduced pressure, and the residue was washed with a hexane:toluene (2:1) solution to afford solid polymerized catalyst: Catalyst IV. ICP-AES: 4.00 mg Fe/g poly.; GPC: Mw 22598, Mn 15406, polydispersity index 1.47. ICP-AES was run with a TJA POEMS ICP analyzer after dry ashing the product and dissolving it in dilute nitric acid).

Olefin Polymerization

Ethylene polymerizations used toluene or hexane as the solvent and also used appropriate ethylene pressure. The polymerization vessel was a 500 mL glass reactor equipped with a propeller-like stirrer. Solvent (100 mL) was introduced into the argon-purged reactor and stirred (800 rpm). The solvent was heated to a prescribed polymerization temperature, and then after, 20 minutes, an ethylene gas feed was started. Adding a toluene solution of cocatalyst (MMAO) and then catalyst (as solid particles or dissolved in toluene) into the reactor with vigorous stirring (800 rpm) initiated polymerization. After a prescribed time, the ethylene gas feed was terminated. Alcohol (500 mL) and concentrated HCl (1 mL) were added to the resulting mixture. The polymer was collected by filtration, washed with methanol (100 mL), and dried in vacuum at 70 °C for 15 hours.

Ethylene polymerization using catalysts I and III in the presence of MMAO dissolved in toluene under one atmosphere of ethylene were investigated. Note that catalyst I is before the catalyst is copolymerized

with a monomer (styrene), while catalyst III is after copolymerization with styrene. The results of ethylene polymerization were summarized:

Table 1: The Result of Ethylene Polymerization[a]

		Catalyst III		Catalyst I	
T(°C)	n(Al)/n(Fe) (molar ratio)	Activity·10^{-6} (g PE / mol·Fe·h)	$M_v \cdot 10^{-4}$	Activity·10^{-6} (g PE / mol·Fe·h)	$M_v \cdot 10^{-4}$
13	550	1.033	15.74	0.644	23.43
13	1100	2.145	15.32	0.916	18.67
13	1650	2.233	11.17	0.959	18.21
13	2200	2.446	6.29	1.588	18.38
13	2750	2.315	7.33	0.984	14.76
13	3300	1.912	6.25	0.627	11.15
-15	2200	5.948	20.59	3.750	24.11
0	2200	4.500	20.11	4.017	20.58
30	2200	2.112	5.46	1.262	8.69
45	2200	1.314	4.92	0.860	8.44
60	2200	0.725	4.86	0.405	4.93

Toluene solvent, 1atm of ethylene, reaction time 1h.

Table 2. Aryl Substituent Effect on Catalyst Performance

Catalyst	M	R	R'	Activity, 10^6 g PE/(mol·M·atm·hr)	Mw
I	Fe	^{i}Pr	^{i}Pr	4.1	8.9×10^4
Ia	Fe	H	H		Low MW
Ib	Fe	Me	Me		Low MW

While certain representative embodiments and details have been shown to illustrate the invention, it will be apparent to skilled artisans that various process and product changes from those disclosed in this application may be made without departing from this invention's scope, which the appended claims define.

All cited patents, test procedures, priority documents, and other cited documents are fully incorporated by reference to the extent that this material is consistent with this specification and for all jurisdictions in which such incorporation is permitted.

Certain features of the present invention are described in terms of a set of numerical upper limits and a set of numerical lower limits. This specification discloses all ranges formed by any combination of these limits. All combinations of these limits are within the scope of the invention unless otherwise indicated.